JOURNAL OF SOLID STATE CHEMISTRY 13, 325–329 (1975)

Phase Behavior of Li_2WO_4 at High Pressures and Temperatures

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Received May 17, 1974

The phase diagram of Li_2WO_4, previously studied by Yamaoka et al. (*J. Solid State Chem.* **6**, 280 (1973)) has been revised. Li_2WO_4 II is stable at atmospheric pressure below ~310°C. This phase appears to be a modified spinel, and is tetragonal, $a, c = 11.941, 8.409$ Å, $Z = 16$, space group $I4_1/amd$. The melting curve of phenacite-type Li_2WO_4 I rises with pressure with a slope of 0.9°C/kbar to the III/I/liquid triple point at 3.1 kbar, 743°C, beyond which the melting curve of orthorhombic Li_2WO_4 III rises steeply with pressure (initial slope 31°C/kbar). The Li_2WO_4 I/III transition line at 3 kbar is almost independent of temperature, i.e., the I/III transition entropy is zero. Li_2WO_4 II is 21.3% denser than Li_2WO_4 I at ambient conditions.

Introduction

The polymorphic behavior of Li_2WO_4 has long been a puzzle. Goldschmidt (*1*) claimed that Li_2MoO_4 and Li_2WO_4, with the phenacite structure at ambient conditions, change to spinel structures at elevated temperature. Later workers could not confirm this. Li_2MoO_4 undergoes no transition up to its melting point at atmospheric pressure (*2*). However, the normal spinel form can be easily prepared by heating the phenacite phase at pressures above ~5 kbar (*3*). In the case of Li_2WO_4, on the other hand, Belyaev (*2*) found a transformation at 660°C, but once again this could not be confirmed (*3, 4*). Dem'yanets (*5*) prepared a new cubic modification of Li_2WO_4 by hydrothermal methods. Very recently Yamaoka et al. (*4*) studied the phase diagram of Li_2WO_4 to 160 kbar and 800°C. They encountered three new high-pressure phases. Orthorhombic Li_2WO_4 III, 21.9% denser than phenacite-type Li_2WO_4 I, is formed above the III/II/I triple point near 665°C, 3 kbar. The II/III phase boundary has a negative slope and terminates at the IV/II/III triple point near 545°C, 13 kbar. The IV/III and II/IV phase boundaries branching off here have slopes of 13 and −83°C/kbar, respectively. The melting curve of Li_2WO_4 rises gently with pressure, with almost no slope increase at the III/I/liquid triple point in spite of the large volume change at the I/III transformation. Li_2WO_4 IV (also orthorhombic) is 2.9% denser than Li_2WO_4 III. The powder pattern of Li_2WO_4 II could not be indexed. None of these phases appeared to be the expected spinel.

It is the object of the present study to clear up some of the remaining discrepancies concerning the phase behavior of Li_2WO_4 at elevated temperatures and pressures.

Experimental

Li_2WO_4 was prepared by repeated firing at 500°C and regrinding of an intimate mixture of reagent grade WO_3 and Li_2CO_3, and also by the dehydration of $Li_2WO_4 \cdot \frac{1}{2}H_2O$ obtained from Hopkin and Williams. The powder patterns of the products were in agreement with reported values.

High-pressure experiments were carried out in a piston–cylinder type apparatus (*6, 7*). Phase changes were studied by means of differential thermal analysis (DTA) and quenching methods, using chromel–alumel thermocouples. The samples were enclosed in

Printed in Great Britain

stainless steel capsules. No reaction between samples and container was noted in the solid state, but after repeated melting–freezing cycles the DTA signals obtained were broadened. Only the first few points obtained in any run were used. Heating/cooling rates used for the DTA experiments ranged from 1.0–1.8°C/sec. The detailed experimental procedure has been described before (*8*, *9*). Pressures are believed to be accurate to better than ±1.0 kbar. Points plotted represent melting temperatures.

Results and Discussion

(*a*) *Crystallography of* Li_2WO_4 *II*[1]

Li_2WO_4 II prepared at 8 kbar, 540°C yielded a powder pattern in excellent agreement with that reported before (*4*). The powder pattern could be indexed on the basis of a tetragonal cell, space group $I4_1/amd\text{-}D_{4h}^{19}$, with $a = 11.941 \pm 0.006$ Å, $c = 8.409 \pm 0.004$ Å, $Z = 16$. The fit to the data is excellent (Table I), and no indication is seen of possible orthorhombic line-splitting.

TABLE I

POWDER PATTERN OF Li_2WO_4 II[a]
(FILTERED CoK_α RADIATION)

d_{obsd} (Å)	d_{calcd} (Å)	$h\,k\,l$	I^b
6.880	6.875	0 1 1	35
5.971	5.971	2 0 0	50
4.507	4.508	2 1 1	86
3.762	3.764	1 1 2	14
3.598	3.598	0 3 1	86
3.437	3.438	0 2 2	88
3.082	3.082	2 3 1	64
2.736	2.738, 2.729	1 4 1, 0 1 3	100 br
2.6708	2.6701	4 2 0	43
2.4818	2.4819	1 2 3	18
2.4340	2.4341	0 4 2	56
2.3403	2.3389, 2.3419	3 3 2, 0 1 5	15
2.2967	2.2974	4 3 1	36
2.2544	2.2540	4 2 2	31
2.1442	2.1441	5 2 1	24 sh
2.1393	2.1396	3 2 3	35
2.1113	2.1109	4 4 0	88
2.1019	2.1023	0 0 4	36 sh
1.9898	1.9902	0 6 0	25
1.8360	1.8368	1 3 4	38
1.8175	1.8179	0 5 3	44
1.7414	1.7415	3 6 1	24
1.6523	1.6518	4 2 4	20
1.6085	1.6099, 1.6080	2 7 1, 6 1 3	30 br
1.5682	1.5679	3 7 0	6
1.5651	1.5671, 1.5644	7 1 2, 5 1 4	18 br
1.5523	1.5527	5 4 3	15
1.5490	1.5492	0 3 5	33
1.5407	1.5408	6 4 2	36
1.5007	1.4996	2 3 5	8
1.4920	1.4926	8 0 0	36 sh
1.4898	1.4896	4 4 4	51
1.4572	1.4572	0 7 3	30 sh
1.4551	1.4544	4 1 5	46
1.3829	1.3826	1 1 6	15
1.3787	1.3787	8 3 1	20
1.3693	1.3692	2 8 2	14
1.3101	1.3106, 1.3095	0 9 1, 7 4 3	14
1.2799	1.2801	7 6 1	7
1.2727	1.2725	8 4 2	18
1.2566	1.2569	3 7 4	15
1.2540	1.2546	3 3 6	18
1.2171	1.2171	0 8 4	13
1.1952	1.1953	0 1 7	13
1.1755	1.1758	6 7 3	14
1.1566	1.1566	5 3 6	11
1.1488	1.1487	0, 1 0, 2	10
1.1120	1.1115	8 1 5	18 sh
1.1097	1.1096	4 1 7	21
1.0759	1.0766, 1.0749	0, 1 1, 1; 8 3 5	21 br
1.0595	1.0595	1 0, 5, 1	12
1.0129	1.0128, 1.0126	1 1, 4, 1; 3 1 8	21

[a] Prepared by heating Li_2WO_4 I for 2 hr at 8 kbar, 540°C.

[b] Sh = shoulder, br = broad.

A comparison with the cell constants of some modified spinels, such as β-Co_2SiO_4 (orthorhombic, *Imma*, *a*, *b*, $c = 5.753$, 11.522, 8.377 Å) (*10*), Zn_2SiO_4 V (orthorhombic, *Imma*, *a*, *b*, $c = 5.740$, 11.504, 8.395 Å), and Zn_2GeO_4 prepared at 72 kbar (tetragonal, $I4_122$ or $I4_322$, *a*, $c = 5.937$, 8.254 Å) (*11*) strongly suggests that Li_2WO_4 II is a further modified spinel with a novel distortion of the

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[1] The designation of phases follows that used in (*4*).

cubic spinel structure due, probably, to the ordering of Li^+ and W^{6+} ions in the octahedral sites of the basic spinel lattice. The volume decrease upon transformation from Li_2WO_4 I to II is 21.3% at 25°C. Li_2WO_4 II is therefore less dense than either Li_2WO_4 III or IV, as confirmed by the phase diagram (*4*). The phenacite/spinel volume change is 21% for Li_2MoO_4 (*3*), quite close to the above value of 21.3% for the phenacite/modified spinel transformation of Li_2WO_4.

(*b*) *Cubic Hydrothermal Li_2WO_4*

This phase, prepared hydrothermally at 400°C, ~1 kbar (*5*), was cubic with $a = 8.30$ Å. However, the selection rules (all allowed) are not consistent with those for spinel. Furthermore, the X-ray density, assuming a spinel structure, is considerably higher even than that of Li_2WO_4 IV—the phase stable at pressures up to 160 kbar (*4*).

Comparison of the powder pattern of this phase with that of $Li_2WO_4 \cdot \frac{1}{2}H_2O$ (*12*) conclusively shows that Dem'yanets prepared $Li_2WO_4 \cdot \frac{1}{2}H_2O$ and not Li_2WO_4. Traces of $Li_2WO_4 \cdot \frac{1}{2}H_2O$ were also present among the products of a run made at 40 kbar, 400°C (*13*), which contained mainly Li_2WO_4 IV.

(*c*) *Stability of Li_2WO_4 II at Atmospheric Pressure*

Upon dehydration of $Li_2WO_4 \cdot \frac{1}{2}H_2O$ in air at low temperatures, we found that the product was often Li_2WO_4 II rather than Li_2WO_4 I. A series of quenching runs were thereupon carried out (Table II). Runs 1–8 clearly indicate that Li_2WO_4 II is the phase stable below 310 ± 110°C, while Li_2WO_4 I is only stable above this temperature. The Li_2WO_4 II $\rightarrow$ I transformation appeared to be considerably more rapid at ~410°C than the reverse Li_2WO_4 I $\rightarrow$ II transformation at ~200°C.

The Li_2WO_4 II/I transformation boundary evidently rises from 310 ± 110°C at atmospheric pressure to the Li_2WO_4 III/II/I triple point somewhere near 3 kbar, 665°C (*4*).

(*d*) *The Transition at 660°C, Atmospheric Pressure*

In the course of a thermal analysis study of the Li_2WO_4–$PbWO_4$ system, Belyaev (*2*)

TABLE II

QUENCHING EXPERIMENTS INVOLVING Li_2WO_4

Run No.	Pressure	Temperature (°C)	Duration	Initial phase	Products
1	Atmospheric	250	24 hr	$Li_2WO_4 \cdot \frac{1}{2}H_2O$	$Li_2WO_4 \cdot \frac{1}{2}H_2O$ +tr · Li_2WO_4 II
2	Atmospheric	280	24 hr	$Li_2WO_4 \cdot \frac{1}{2}H_2O$	Li_2WO_4 II +$Li_2WO_4 \cdot \frac{1}{2}H_2O$
3	Atmospheric	350	24 hr	$Li_2WO_4 \cdot \frac{1}{2}H_2O$	Li_2WO_4 II
4	Atmospheric	400	24 hr	Li_2WO_4 II	Li_2WO_4 II
5	Atmospheric	420	24 hr	Li_2WO_4 II	Li_2WO_4 I
6	Atmospheric	550	24 hr	Li_2WO_4 II	Li_2WO_4 I
7	Atmospheric	250	2 wk	Li_2WO_4 I	Li_2WO_4 I
8	Atmospheric	200	4 wk	Li_2WO_4 I	Li_2WO_4 I +trace Li_2WO_4 II
9	Atmospheric	800	1 hr	Li_2WO_4 I	Li_2WO_4 I +$Li_2W_2O_7$
10	8 kbar	500	24 hr	Li_2WO_4 I	Li_2WO_4 II
11	12 kbar	700	1 hr	Li_2WO_4 I	Li_2WO_4 III
12	32 kbar	700	1 hr	Li_2WO_4 I	Li_2WO_4 IV
13	8 kbar	540	2 hr	Li_2WO_4 I	Li_2WO_4 II

detected a transformation in Li_2WO_4 (0% $PbWO_4$) at 660°C. This has not been confirmed by other workers (*3*, *4*). A DTA run on pure contained Li_2WO_4 in the present study also failed to reveal any DTA signal near 660°C. It was found, however, that if Li_2WO_4 is heated to well above its melting point at atmospheric pressure, some loss of Li_2O occurs by evaporation, yielding a mixture of Li_2WO_4 and $Li_2W_2O_7$ as the run products (Table II, Run 9).

Pure $Li_2W_2O_7$ was therefore prepared from a suitable mixture of Li_2CO_3 and WO_3 by repeated heating to 500°C and regrinding. The powder pattern was indexed on the basis of a triclinic cell with $a = 8.261 \pm 0.008$ Å, $b = 7.035 \pm 0.007$ Å, $c = 5.047 \pm 0.005$ Å, $\alpha = 85.37°$, $\beta = 102.15°$, $\gamma = 110.29°$, $Z = 2$. These values are in good agreement with, but more precise than, the cell recently reported by Magarill (*14*).

$Li_2W_2O_7$ was found to exhibit a sharp and reversible phase transformation with a large latent heat at 666.6 ± 1.5°C and atmospheric pressure. It is therefore suggested that the heat events observed by Balyaev (*2*) at this temperature were due to the presence of some $Li_2W_2O_7$ formed by loss of Li_2O during the foregoing excursions above the melting point of Li_2WO_4.

(*e*) *Melting Curves of Li_2WO_4 I and III*

The melting curve of Li_2WO_4 reported previously (*4*) rises smoothly from ~740°C at atmospheric pressure to ~820°C at 33 kbar, with no inflection noted at the Li_2WO_4 III/I/liquid triple point, presumably near 3 kbar. The Li_2WO_4 I/III transition involves a volume decrease of 21.9% (*4*), and an extremely drastic increase in slope should occur at the triple point.

Samples for DTA runs at high pressures were contained in nickel, Monel and stainless steel capsules. Sample/capsule reaction was encountered in all cases, but in the case of stainless steel did not noticeably affect the melting temperature observed until ten or more melting/freezing cycles had been completed. Stainless steel was therefore used as container material, and only the first few points obtained in any given run were measured. The results are shown in Fig. 1.

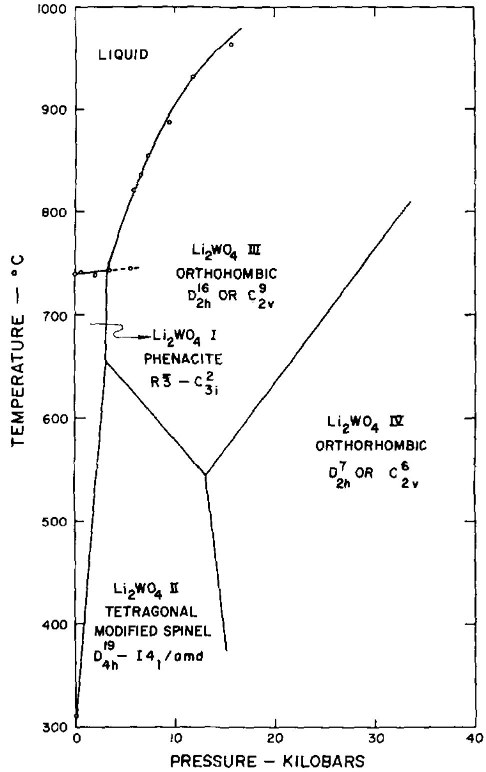

FIG. 1. Phase diagram of Li_2WO_4. The II/III, II/IV and IV/III phase boundaries are taken from Ref. (*4*). The I/II equilibrium temperature at atmospheric pressure has an uncertainty of ±110°C.

The melting curve of Li_2WO_4 I rises with pressure with an initial slope of 0.9°C/kbar, and its metastable extension was followed to 7.5 kbar, well past the Li_2WO_4 III/I/liquid triple point. Above ~7.5 kbar the melting points discontinuously jump to higher temperatures due to the occurrence of the Li_2WO_4 I/III transformation. The melting curve of Li_2WO_4 III rises steeply with pressure from the III/I/liquid triple point at 3.1 kbar, 743°C (by extrapolation) with an initial slope of 31°C/kbar.

Attempts were made to obtain one or more points on the metastable extension of the Li_2WO_4 IV melting curve to lower pressures and temperatures by converting the sample to Li_2WO_4 IV at ~650°C, 30 kbar, reducing pressure rapidly and then heating. However, the rate of transformation to stable Li_2WO_4 III appeared to be relatively high near the

TABLE III

PHASE BOUNDARIES OF Li_2WO_4

Phase boundary	Fit (P in kbar)	SD
II/I[a]	$t(°C) = 310 + 120\,P$	—
I/III[a]	$P = 3$	—
II/III[b]	$t(°C) = 665 - 12\,(P - 3)$	—
II/IV[b]	$t(°C) = 545 - 83\,(P - 13)$	—
IV/III[b]	$t(°C) = 545 + 13\,(P - 13)$	—
I/liq	$t(°C) = 740 + 0.89\,P$	1.6°C
II/liq	$t(°C) = 743 + 30.8\,(P - 3.1) - 1.05\,(P - 3.1)^2$	3.0°C

Triple point	Pressure (kbar)	Temperature (°C)
III/II/I[b]	~3	665
IV/II/III[b]	13	545
III/I/liq	3.1 ± 0.8	743 ± 2

[a] Approximate.

[b] From Ref. (*4*).

melting lines and only the melting of Li_2WO_4 III was observed.

The phase relations of Li_2WO_4 are summarized in Table III.

(*f*) *Thermodynamic Quantities*

Application of the Clapeyron–Clausius equation and use of the known slopes and volume changes allow us to calculate some approximate thermodynamic transition properties. We find:

$$\Delta S_{\mathrm{II/I}} \simeq 10 \text{ J/mole deg}$$
$$\Delta S_{\mathrm{I/III}} \simeq 0$$

Then, from the earlier value of $\Delta V_{\mathrm{I/III}}$ (*4*) and the present relations at the III/I/liq triple point, assuming $\Delta S_{\mathrm{I/liq}}$ to be approximately constant along the short melting curve of Li_2WO_4 I,

$$\Delta S_{\mathrm{I/liq}} \simeq 40 \text{ J/mole deg}$$
$$\Delta V_{\mathrm{I/liq}} \simeq 0.4 \text{ cm}^3\text{/mole (at } P = 0)$$
$$\Delta S_{\mathrm{II/liq}} \simeq 40 \text{ J/mole deg (at } P = 3 \text{ kbar)}$$
$$\Delta V_{\mathrm{II/liq}} \simeq 13 \text{ cm}^3\text{/mole (at } P = 3 \text{ kbar).}$$

The entropy changes at the II/III, II/IV and IV/III transformation lines could in principle be calculated in the same way, but since no data are available concerning the differential compressibilities and thermal expansion coefficients of these phases, large errors may result in view of the small density differences between Li_2WO_4 II, III, and IV.

Acknowledgments

The author wishes to thank Martha C. Pistorius who wrote the computer programs used, J. Erasmus and his staff, and A. de Kleijn and his staff who kept the apparatus in good repair, and were responsible for the manufacture of the furnace parts. Calculations were carried out on the IBM System 360/65H of the National Research Institute for Mathematical Sciences.

References

1. V. M. Goldschmidt, *Skr. Akad. Oslo* **2**, 107 (1926).
2. I. N. Belyaev, *Russ. J. Inorg. Chem.* **6**, 602 (1961).
3. J. Liebertz and C. J. M. Rooymans, *Solid State Comm.* **5**, 405 (1967).
4. S. Yamaoka, O. Fukunaga, T. Ono, E. Iizuka, and S. Asami, *J. Solid State Chem.* **6**, 280 (1973).
5. L. N. Dem'yanets, *Sov. Phys. Cryst.* **13**, 741 (1969).
6. G. C. Kennedy and R. C. Newton, *In* "Solids under Pressure" (W. Paul and D. M. Warschauer, Eds.), McGraw–Hill, New York, 1963.
7. G. C. Kennedy and P. N. Lamori, *In* "Progress in Very High Pressure Research" (F. P. Bundy, W. R. Hibbard, and H. M. Strong, Eds.), p. 304. Wiley, New York, 1961.
8. C. W. F. T. Pistorius and J. B. Clark, *High Temp. High Press.* **1**, 561 (1969).
9. P. W. Richter and C. W. F. T. Pistorius, *J. Solid State Chem.* **3**, 197 (1971).
10. M. Tokonami, N. Morimoto, S. Akimoto, Y. Syono, and H. Takeda, *Earth Planet. Sci. Letters* **14**, 65 (1972).
11. Y. Syono, S. Akimoto, and Y. Matsui, *J. Solid State Chem.* **3**, 369 (1971).
12. H. E. Swanson, M. C. Morris, R. P. Stinchfield, and E. H. Evans, *Natl. Bur. Stand. (U.S.) Mon.* **25–2**, 20 (1963).
13. C. J. M. Rooymans, personal communication.
14. S. A. Magarill, R. F. Klevtsova, and V. V. Bakakin, *Krist.* **18**, 269 (1973).